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Synthesis and application of photo curable perfluoropolyethers as new material for microfluidics

C. Hannig[a], M. Dirschka[a], K. Länge[a], S. Neumaier[b], B. E. Rapp[a]

[a]*Institute for Microstructure Technology (IMT), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

[b]*Institute of Functional Interfaces (IMT), Karlsruhe Institute of Technology (KIT)), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

Abstract

We will describe the use of an alternative polymer which is suitable for use in microfluidic applications which require the use of harsh chemicals or aggressive solvents. Currently microfluidics systems are mainly manufactured in polydimethylsiloxane (PDMS) due to its ease of use, and the ability to produce monolithic microfluidic valves directly into the same material as the microfluidic chip. However, PDMS has limitations with respect to its chemical stability as it swells in contact with a lot of solvents and tends to become brittle when exposed to substances such as tetradecane. Polymers synthesized from perfluoropolyethers (PFPE) have significant advantages due to their outstanding chemical stability. Furthermore it is possible to photo cure these polymers allowing the convenient structuring of these polymers via lithography. We will demonstrate first experimental result in producing microfluidic components and their application with these polymers.

Keywords: microfluidics, polymers, droplet microfluidics, synthesis, biosensors

1. Introduction

Microfluidics is the key element for the design of market compatible sensor biosensor system as well as a crucial part of all microfluidic systems designed for synthesis or chemical analysis [1].

Conventionally microfluidic components have been developed as singular components, detached from the application specific layout of a microfluidic system. The main component being developed are microfluidic pumps [2] and valves [3]. Multiple of these components are then integrated onto a microfluidic chip resulting in highly integrated systems [4, 5]. The main drawback of this strategy is the fact that micropumps and microvalves with integrated actors usually expose various materials to the liquids in the microfluidic system resulting in contamination of the samples. In addition, if single use components are required, as it is the case for most biomedical applications, the systems have to be disposed after each experiment resulting in significant increase of the overall costs.

There are several ways to overcome this problem. By means of an intermediary liquid it is possible to avoid direct contact of the expensive components and the sample resulting in an indirect microfluidic system [6, 7]. Another way is to use soft materials that allow the creation of microfluidic valves intrinsically due to the material's elasticity.

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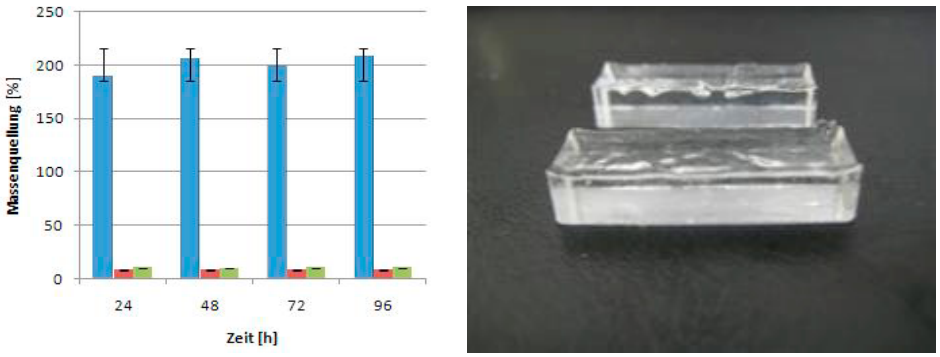

Fig 1: left - chemical resistance demonstrated by the swelling behavior of PFPE based polymers (red and green bars, two batches of the same polymer) and PDMS (blue bar) when exposed to dichloromethane for up to 96 hours (mean value of the mass increase with error bars determined from 3 samples); right - solid block of cured PFPE polymers used for the evaluation of the swelling behavior of the polymer when immersed in commonly used solvents such as dichloromethane, acetone or 2-propanol

Today these microfluidics systems are usually created in polydimethylsiloxane [8-10]. One major drawback of almost all systems found in literature is the fact that PDMS has its limitation due to the restricted chemical resistance especially to solvents such as tetradecane or dichloromethane. Even water will result in swelling of the polymer [11].

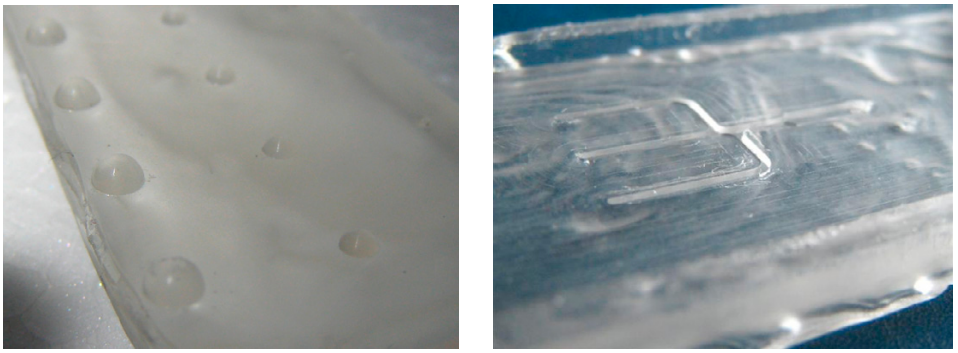

Fig 2: left - semi-spheres produced from PFPE polymers via curing against a mechanically structured brass molding tool; right - double T junction structure produced from PFPE polymers replicated from a mechanically structured polytetrafluoroethylene (PTFE) master. The structure can be used as droplet generator junction for droplet microfluidic applications.

2. Photo curable perfluoropolyethers PFPE polymers

Using polymers synthesized from PFPE has been suggested as an alternative way to the creation of materials suitable for microfluidic applications [12, 13]. These polymers feature outstanding chemical resistance and biocompatibility due to the high concentration of fluoro on the monomer main chain (data not shown). In many ways these polymers can be regarded as equivalents to classical polytetrafluoroethylene (PTFE) with a couple of main advantages compared to PTFE:

- The monomer can be designed in a way that it is photo curable resulting which allow the photo structuring of components by means of classical lithographic methods.

- The resulting polymers are transparent which allows the creation of components that can be used in optical spectroscopy and similar methods.
- By modifying the photo curing process by changing the amount of photo initiator the resulting mechanical properties (Young's modulus, hardness, color) can be changed in a wide range.

However, the synthesis protocols described in literature so far did not include the purification of the monomers after the synthesis which is required in order to obtain polymers with good chemical properties. We have modified the protocols described in literature resulting in an easy and convenient way to create and purify the monomers as well as subsequently cure them via exposure to UV light (see fig. 1, 2). We will describe the synthesis protocols and show first experimental results obtained with these polymers.

3. Application range: droplet microfluidics

One potential and interesting application scope for PFPE polymers is droplet microfluidics (see fig. 3). The creation of droplets of aqueous phases in an immiscible second stream of an oil is easier if the contact angle of the material in which the channels are contained. As PFPE polymers have a static contact of about 110° against water and very low surface tension (below 10 mN/m), they can be used to stably create streams of droplets for a very long period (several hours) without the risk of water sticking to the wall of the channels, which can occur with PDMS microfluidic chips (see fig. 4)

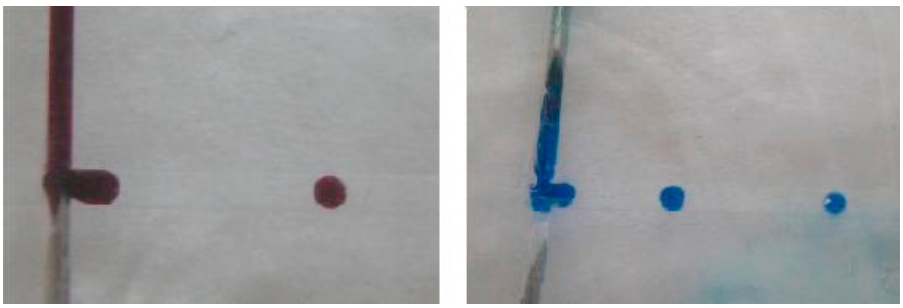

Fig 3: Droplets created at the intersection of two fluidic channels manufactures in PFPE polymers (diameter of the channels 1.6 mm respectively), aqueous phase: water with dye, oil phase: FC-40. The images were taken after the respective experiment has been running for 4 hours. In the course of the experiment, no attachment of droplets to the wall occurred, the continuous stream of droplets is not ruptured. No surfactants have to be used.

Flow rate aqueous phase [µl/min]	Flow rate oil phase [µl/min]	Droplet size, PFPE polymers [µl]	Droplet size, PDMS polymers [µl]
246.91	3 000	1.5	1.5
246.91	4 000	1.25	1.25
246.91	6 000	1.005	1.005
246.91	7 500	0.9	0.94
246.91	12 000	0.5	No stable droplet stream
246.91	20 000	0.45	No stable droplet stream

Tab 1: Comparative results of PDMS and PFPE microfluidic chips and obtained volumes of droplets in continuous droplet streams created at the cross section of two fluidic channels (1.6 mm diameters respectively). The data shows that the size of the created droplets can be effectively varied by varying the flow rates of the oil phase or the aqueous phase (data not shown). As the droplet size is decreased below 0.9 µl volume per droplet, the stability of the droplet streams created in the PFPE microfluidic chip is much higher due to the lower sticking of droplets the channel walls as a consequence of the lower surface tension. The creation of stable streams of droplet becomes impossible in PDMS microfluidic channel at droplet sizes below 0.95 µl.

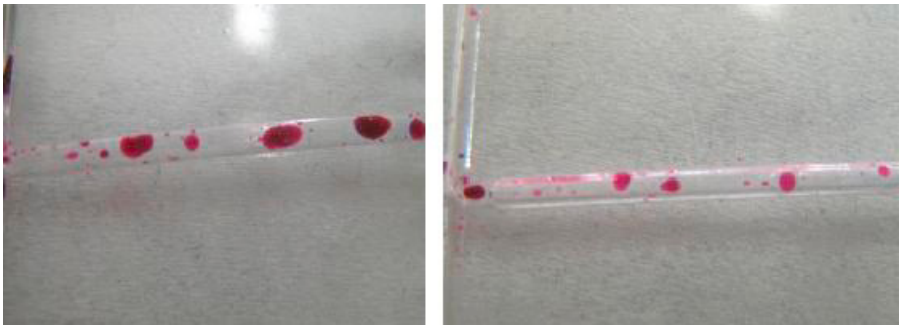

Fig 4: Droplets created in a 1.6 mm diameter microfluidic channel in PDMS (aqueous phase: water with dye, oil phase: FC-40). The image was taken after the experiment has been running for 4 hours. In the course of the experiment, droplets of water attach to the wall thus rupturing the continuous stream of droplets and effectively stopping the experiments. This can usually only be prevented by using surfactants.

We have created junctions of fluidic channels in PDMS and PFPE polymers for comparative experiments. Within these channels the creation of droplets of defined volumes was evaluated. Creating stable droplet streams of volumes below 1 µl has proven to be difficult in PDMS microfluidic channels (see fig. 4 and table 1) due to the tendency of the droplets to attach the channel walls. This did not occur in PFPE microfluidic channels resulting in stable streams of small droplets over experimental runs of several hours.

4. Conclusion

PFPE polymers are a versatile alternative for applications in microfluidics. We will demonstrate simple and robust synthesis protocols as well as extended application data and experimental results with this new type of polymers.

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